



KINETIC MECHANISM REDUCTION FOR METHYL FORMATE THROUGH DEPTH FIRST SEARCH AND SENSITIVITY ANALYSIS

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Abstract. Biodiesel has been considered the most promising fuel to replace part of the fossil diesel consumed worldwide, since it is a renewable and biodegradable fuel. There is the need of reduced kinetic mechanisms for the effective numerical simulation of these fuels. In this way, the aim of this work is the development of a reduced mechanism of moderate stiffness for Methyl Formate (MF). MF is not indicated as a biodiesel surrogate due to its higher reactivity, but its study enables to isolate the role of each ester in combustion processes. So, based on a detailed mechanism consisting of 950 reactions and 176 species, Directed Relation Graph with Depth First Search and Sensitivity Analysis are employed to obtain a small mechanism with 43 reactions and 23 species for MF. This mechanism has reasonable accuracy compared to the full mechanism and decreases the computational cost for obtaining the solution of the reactive flow.

Keywords: Biodiesel, Methyl Formate, Mechanism Reduction, Sensitivity Analysis

1 INTRODUCTION

Combustion has always been present in human life for energy conversion, trigger transportation, fire prevention systems, pollution control, processing materials, etc (Ferziger, 2002). The energy conversion processes increasingly tend to take into account economic and environmental constraints. The need to reduce the consumption of petroleum, the search for alternative energy sources, and the increasing emission of pollutants, makes the combustion a research area in great expansion (Alim, 2005). Thus, it becomes necessary to have a better understanding and control of the interaction between combustion and turbulence, since we can control the emission of pollutants, stability, combustion noise and fuel efficiency.

Biodiesel has been considered the most promising fuel to replace part of fossil diesel consumed in the world. It is a mixture of methyl esters or ethyl fatty acids obtained by transesterification of some triglycerides, using a small chain alcohol such as methanol or ethanol.

The advantages of using biodiesel is that it is a renewable biodegradable fuel, whose production originates opportunities of job creation in the primary and industrial sectors. Using biodiesel instead of there is a significant and quantitative reduction of pollution levels, resulting in reduced emission of particulates.

The evaluation of the quality of fuel oils requires the analytical determination, especially of its calorific value, cetane index, distillation curve, viscosity and cloud point. A thermodynamic study of combustion allows to optimize the process of burning and to reduce atmospheric pollution, the maximum reusing of residues solids, and facilitates the construction of ever more efficient machines.

There are studies showing that small methyl esters exhibit distinctive laminar flame burning velocities and different CO_2 evolution histories. However, these differences are small (10%) compared to the experimental uncertainties order (Farooq et al., 2009 and Wang et al., 2011).

The goal of this work is to simulate the combustion of methyl formate based on a reduced kinetic mechanism. The reduction strategies applied are the Directed Relation Graph (DRG), with Depth First Search (DFS). Some sort of Sensitivity Analysis is also applied to the skeletal mechanism developed by DRG/DFS to further eliminate species and reactions. The advantage of using these methods is the elimination of redundant species and reactions, decreasing the computational cost needed to solve the chemical system of equations, of about one order of magnitude for MF.

2 METHYL FORMATE

Methyl formate (CH_3OCHO) is the simplest methyl ester. Westbrook (2009) developed and validated a detailed kinetic model for MF combustion for fuel rich, low pressure, premixed laminar flames. The detailed kinetic MF oxidation model discussed and validated by Dooley et al. (2010, 2011) agrees well with different experimental measurements obtained in the Princeton University pressurized flow reactor, and in the Galway shock tube device for low pressure premixed laminar flames.

Methyl formate is mainly converted to methanol and CO (Grana et al., 2012): formaldehyde and methane are major intermediate species, while smaller amounts of ethylene and acetylene are also formed, via methyl radical recombination reactions that occur at high temperatures and fuel rich conditions.

Diévar et al. (2013) conducted an interesting study on diffusive extinction limits of a series of methyl ester flames, from methyl formate to methyl decanoate, using the counterflow configuration. For a diffusion flame condition, hydrogen abstraction reactions account for only 60% of MF consumption, producing the CH_3OCO (18%) and CH_2OCHO (42%) radicals. These two radicals further decompose to produce either $\text{CH}_3 + \text{CO}_2$ or $\text{CH}_3\text{O} + \text{CO}$ (CH_3OCO) and $\text{CH}_2\text{O} + \text{HCO}$ (CH_2OCHO). The remaining MF fraction (35%) is consumed by molecular decomposition to form methanol and CO . The Figure 1 shows the consumption pathways of the fuel and the radicals formation.

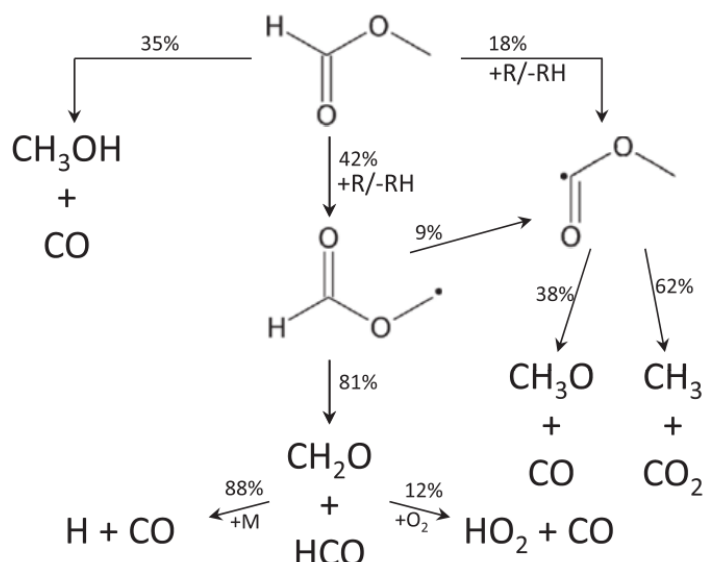


Figure 1: Methyl formate oxidation in a diffusion flame (adapted from Diévar et al., 2013).

These studies show that methyl esters smaller than methyl butanoate cannot be used as biodiesel surrogates, to emulate the high temperature flame chemistry, due to their distinctive reaction kinetics. Nevertheless, detailed understanding of the reaction kinetics of small methyl esters is crucial to the development of a reliable kinetic model for larger methyl esters and biodiesels.

Since methyl formate is one of the simplest biodiesel constituents, its study allows to isolate the role of each ester functionality in combustion processes. Knowing that the analysis employing detailed kinetic mechanisms is complicated by the existence of highly reactive radicals that induce a significant rigidity to the system, the aim of this work is the development of the corresponding reduced kinetic mechanisms of less variables and moderate stiffness.

3 OBTAINMENT OF A REDUCED MECHANISM FOR THE METHYL FORMATE COMBUSTION

The techniques of reduction of chemical mechanisms can be classified in terms of global reduction in the number of reactions, and of refinement of the mechanism.

Simplified mechanisms are usually adopted to describe combustion processes. Thus, one can reduce the rigidity of the system of equations, the size of the mechanism, and hence the computational time of processing and data storage necessary for the numerical simulation (Apte and Yang, 2002, Andreis et al. 2013).

3.1 Directed Relation Graph

According to Lu and Law (2006), to obtain a skeletal mechanism one identifies and eliminates unimportant reactions or species. Typically, the identification of unimportant species is more relevant than that of reactions, due to the complex coupling of the species. The method DRG was developed to identify the species coupling efficiently, which indicates that the removal of one species B from the mechanism induces immediate error to the production rate of a species A . Such index, noted as r_{AB} , can be expressed as:

$$r_{AB} = \frac{\sum_{k=1,I} |\nu_{A,k} \omega_k \delta_{B,k}|}{\sum_{k=1,I} |\nu_{A,k} \omega_k|} \quad (1)$$

where the subscripts A e B indicate the species, k is the k th reaction, $\nu_{A,k}$ the stoichiometric coefficient of species A in the k th reaction, ω_k the reaction rate and $\delta_{B,k}$ is given by:

$$\delta_{B,k} = \begin{cases} 1 & , \text{ if the } k\text{th elementary reaction involves species } B, \\ 0 & , \text{ otherwise.} \end{cases} \quad (2)$$

The terms in the denominator of the Eq. (1) are the contributions of the reactions to the production rate of species A , and the terms in the numerator are those in the denominator that involve species B . If the relative error r_{AB} is not small compared to a threshold value ε , the removal of species B from the skeletal mechanism immediately induces a nonnegligible error in species A . Consequently, species B should be kept in the skeletal mechanism if species A is to be retained. Such requirement of species A to species B is denoted by $A \rightarrow B$.

The dependent set of major species can be identified by mapping the species coupling with Directed Relation Graph, using the following rules:

- (1) Each vertex in DRG is uniquely mapped to a species in the detailed mechanism;
- (2) There exists a directed edge $A \rightarrow B$ if and only if $r_{AB} \geq \varepsilon$;
- (3) The starting vertices of DRG correspond to the major species in the mechanism.

The Figure 2 shows the typical relations between the species (vertices) in DRG. The arrow shows the direction of dependence of one species on another, with its width indicating the strength of dependence.

Thus, for each species A , there exists a group of species, which are reachable from A , and this set of species is defined as the dependent set of A , denoted as S_A . If species A is an important species to be kept in the skeletal mechanism, its dependent set S_A should be kept as well (Lu and Law, 2005).

3.2 Depth First Search

Depending on the threshold parameter value ε , flaws in the mechanism obtained by the DRG and related techniques may appear. Therefore, it is convenient to use this technique with a search algorithm for graphs, DFS for example as shown in the Figure 3, to establish the species of the main chain (Cormen, 2001). In this case, for each starting species A of the graph, is applied the method DFS to identify the set S_A .

The elementary reactions of the skeleton mechanism can be obtained by eliminating all

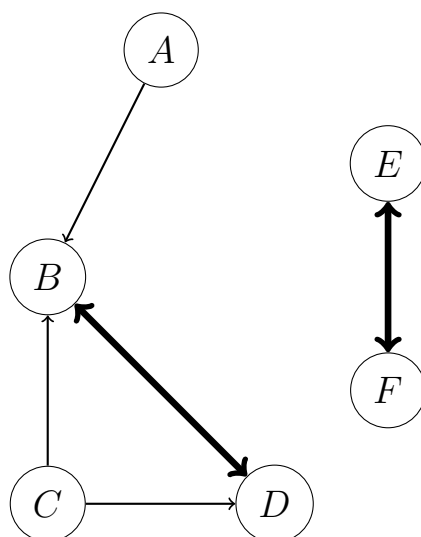


Figure 2: Typical configuration of the DRG (Lu and Law, 2005).

elementary reactions of the detailed mechanism that does not depends on any species of the skeletal mechanism.

It is noted that the set of starting vertices does not need to contain every major species in the mechanism. Instead, in most cases, it is sufficient to start with a single species, such as the fuel, to identify all the species in the skeletal mechanism. This is because the other major species such as the oxidizer, the products, and the major radicals are required by the fuel either directly or indirectly, and as such they can be retained together with the other important species automatically in the DFS technique. In cases in which multiple starting vertices are required, the DFS technique can be applied to each starting vertex and the collection of all discovered vertices constitutes the species set of the skeletal mechanism (Lu and Law, 2006).

The main advantage of using the DFS technique is that it allows, among the many possible routes to obtain a reduced mechanism, to establish the main path to determine the principal combustion products (H_2O , CO_2 , CO and H_2). The species related to the main path can be used as target species when using the DRG techniques, reducing the computational effort to obtain the skeletal mechanism (De Bortoli et al., 2015).

3.3 Sensitivity Analysis

Sensitivity analysis consists in computing derivatives of one or more quantities (outputs) with respect to one or several independent variables (inputs). Since the calculation of gradients is often the most costly step in the optimization cycle, using efficient methods that accurately calculate sensitivities is extremely important (Martins, 2002).

According to Lebedev et al. (2012), there are several types of sensitivity matrices: a concentration sensitivity matrix, a rate sensitivity matrix, and a Jacobian matrix. Concentration sensitivity matrix is the sensitivity of species concentrations with respect to reaction rate constants. The components of the concentration sensitivity matrix \hat{S} and of the normalized concentration

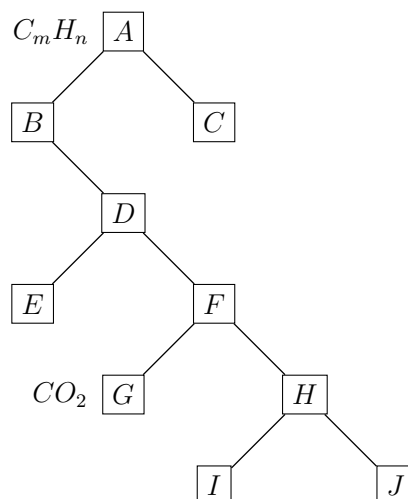


Figure 3: A DFS scheme (De Bortoli et al., 2015).

sensitivity matrix \mathbf{S} are given by, respectively:

$$\hat{S}_{ij} = \frac{\partial c_i}{\partial k_j} \quad (3)$$

$$S_{ij} = \frac{k_j}{c_i} \hat{S}_{ij} = \frac{k_j}{c_i} \frac{\partial c_i}{\partial k_j} \quad (4)$$

The value of the sensitivity coefficient of substance i related to the rate constant of reaction j corresponds to the variation of the concentration of species i after a small change of the rate constant of reaction j . Therefore, the reaction j should be considered important if at least one of the important species has large sensitivity with respect to this reaction.

Direct Sensitivity Analysis

In the Direct Sensitivity Analysis (DSA) method, the maximum value of the sensitivity of concentration to each reaction is calculated and compared with the threshold value (Deminsky et al., 2003). The principal characteristics of this method are:

- i) These is a threshold value (controlling parameter);
- ii) The reactions with all sensitivity coefficients smaller than the threshold value are excluded from the mechanism.

The input of the method consists of the sensitivity matrix given by:

$$S_{ij} = \frac{k_j}{c_i} \frac{\partial c_i}{\partial k_j} = \frac{\partial \ln c_i}{\partial \ln k_j} \quad (5)$$

The importance index I_m of the reaction m is equal to the maximum value of sensitivity coefficients $S_{A,m}$, as shown in the Figure. 4. The index I_m is not normalized and can take any value greater than zero. Once each I_m is found, the importance index values of all reactions are compared with the threshold value. By default, the threshold value is equal to 1.

In the Figure 4, \mathbf{S} is the sensitivity matrix, threshold corresponds to the value defining important reactions, m denotes the reaction under analysis, A corresponds to species of the mechanism, and I_m is the importance index of reaction m .

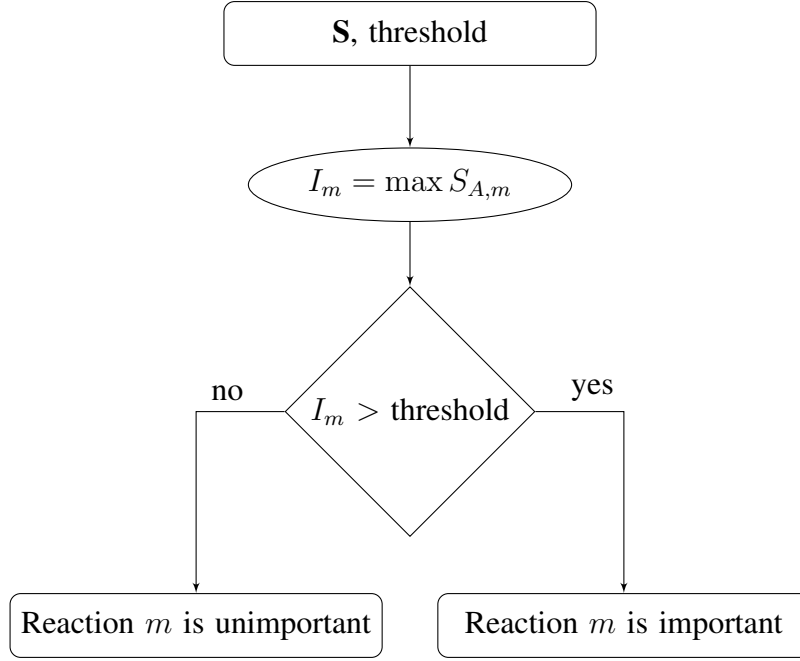


Figure 4: Scheme of the method Direct Sensitivity Analysis (DSA) (Lebedev et al., 2012).

If the index I_m is greater than the threshold, the reaction m is considered important. Otherwise, the reaction is not considered important. The skeletal mechanism is derived from the detailed mechanism by keeping only important reactions.

4 FLOW EQUATIONS FOR DIFFUSION FLAMES

The major advantage in working with reduced mechanisms is the decrease in the computational cost needed to solve the chemical set of equations, of about one order of magnitude for MF. Moreover, when solving diffusion flames is required the solution of equations for momentum, temperature (here obtained using the mixture fraction) (Kuo and Acharya, 2012) species mass fractions, density and pressure. These equations are:

$$\frac{\partial(\rho v_i)}{\partial t} + \frac{\partial(\rho v_i v_j)}{\partial x_j} = \frac{\partial p}{\partial x_i} + \frac{\partial \sigma_{ij}}{\partial x_j}, \quad (6)$$

$$\frac{\partial(\rho Z)}{\partial t} + \frac{\partial(\rho v_j Z)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\rho D \frac{\partial Z}{\partial x_j} \right). \quad (7)$$

where, t is time, v the velocity, p the pressure, Z the mixture fraction (to obtain the temperature) and D the molecular diffusivity.

The temperature is obtained using the analytical solution of Burke-Schumann, in which:

$$T_b = \begin{cases} T_u + \frac{QY_{F,1}}{c_p v_F' W_F'}, & \text{if } Z \leq Z_{st}; \\ T_u + \left(\frac{QY_{O_2,2}}{c_p v_{O_2}' W_{O_2}} \right) (1 - Z), & \text{if } Z \geq Z_{st} \end{cases} \quad (8)$$

The mass fraction of species is obtained by solving:

$$\frac{\partial(\rho Y_k)}{\partial t} + \frac{\partial(\rho v_j Y_k)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\rho D_t \frac{\partial Y_k}{\partial x_j} \right) + \dot{W}_k. \quad (9)$$

where, Y_k is the mass fraction of species k and \dot{W}_k is the term that accounts for the consumption or generation of species k , which results from the reaction rate that involves species k .

The density ρ is obtained using the equation of state for ideal gas, $\rho = p/RT$, and the pressure comes from the equation (Pitsch and Steiner, 2000):

$$\nabla^2 p = \Delta t \left(\frac{\partial v_i}{\partial x_i} + \frac{\partial \rho}{\partial t} \right). \quad (10)$$

5 OBTAINED RESULTS AND DISCUSSION

Fisher et al. (2000) were the first to present a detailed mechanism for MF with 950 reactions and 176 species. This mechanism was used to perform the reduction in this work.

After applying the technique DRG in the original mechanism, with $\varepsilon = 0.1$, it results 116 reactions and 56 species. For the DFS method, we use as target species: CH_2OCHO , CH_3OCHO , CH_3OCO , CH_3O , HCO , CH_3 , HO_2 , H_2O_2 , CH_3OH , O , H_2O , CO_2 , H , O_2 and CO , to choose which reactions remain in the skeleton mechanism. After this procedure, remained 92 reactions and 43 species. The final mechanism obtained with DSA method, whose threshold is given by 0.23, consists of 43 reactions and 23 species. The reactions of the reduced mechanism for MF are presented in the Table 1.

Table 1: Reactions that involve the reduced mechanism for MF; units are mol, cm^3, s, K and cal/mol .

Number	Reaction	A	β	E
1	$CH_3OCHO + OH = H_2O + CH_2OCHO$	0.52E+10	0.97	1590
2	$HCO + OH = CO + H_2O$	0.10E+15	0.00	0
3	$CO + OH = CO_2 + H$	0.14E+00	1.95	-1347
4	$CH_2 + H = CH + H_2$	0.10E+19	-1.56	0
5	$CH_3OCHO + CH_3O = CH_3OH + CH_2OCHO$	0.16E+12	0.00	7000
6	$CH_3OCHO + HO_2 = H_2O_2 + CH_2OCHO$	0.84E+13	0.00	20440
7	$CH_3OCHO + H = H_2 + CH_3OCO$	0.65E+06	2.40	4471
8	$CH_3OCHO + O_2 = HO_2 + CH_2OCHO$	0.30E+14	0.00	32800
9	$CH_3OCHO + HO_2 = H_2O_2 + CH_3OCO$	0.28E+13	0.00	17690
10	$CH_3OCHO + O_2 = HO_2 + CH_3OCO$	0.10E+14	0.00	31050
11	$CH_3OCHO + OH = H_2O + CH_3OCO$	0.23E+08	1.61	-35
12	$CH_3OCHO + OH = H_2O + CH_2OCHO$	0.52E+10	0.97	1590
13	$CH_2OCHO = CH_3OCO$	0.26E+12	-0.03	38180
14	$CH_3OCO + HO_2 = OH + CH_3O_2 + CO$	0.70E+13	0.00	-1000
15	$CH_3OCO + CH_3O_2 = CH_3O + CH_3O_2 + CO$	0.70E+13	0.00	-1000

Table 1: (continued)

Number	Reaction	A	β	E
16	$CH_3OCO + H = CH_3OCHO$	0.10E+15	0.00	0
17	$CH_3O_2 + CH_3 = CH_3O + CH_3O$	0.70E+13	0.00	-1000
18	$C_2H + O_2 = HCO + CO$	0.24E+13	0.00	0
19	$CH_3 + OH = CH_2O + H_2$	0.22E+14	0.00	4300
20	$CH_3 + H = CH_2 + H_2$	0.90E+14	0.00	15100
21	$CH_3 + OH = CH_2 + H_2O$	0.30E+07	2.00	2500
22	$CH_2 + OH = CH + H_2O$	0.11E+08	2.00	3000
23	$CH_3OH + OH = CH_2OH + H_2O$	0.71E+07	1.80	-596
24	$CH_3OH + H = CH_3O + H_2$	0.36E+13	0.00	6095
25	$CH_3O + O_2 = CH_2O + HO_2$	0.55E+11	0.00	2424
26	$CH + O_2 = HCO + O$	0.33E+14	0.00	0
27	$CH_2OH + M = CH_2O + H + M$	0.28E+15	-0.73	32820
28	$CH_2O + H = HCO + H_2$	0.93E+09	1.50	2976
29	$CH_2O + O = HCO + OH$	0.42E+12	0.57	2762
30	$CH_2O + OH = HCO + H_2O$	0.34E+10	1.18	-447
31	$HCO + H = CO + H_2$	0.73E+14	0.00	0
32	$HCO + HO_2 = CH_2O + O_2$	0.30E+11	0.33	-3861
33	$CO + HO_2 = CO_2 + OH$	0.30E+14	0.00	23000
34	$CO + CH_3O = CH_3OCO$	0.15E+12	0.00	3000
35	$H_2O_2 + OH = H_2O + HO_2$	0.10E+13	0.00	0
36	$H_2O_2 + O_2 = HO_2 + HO_2$	0.59E+18	-0.66	53150
37	$H_2O_2 + H = H_2 + HO_2$	0.48E+14	0.00	7950
38	$H_2O_2 + H = H_2O + OH$	0.24E+14	0.00	3970
39	$HO_2 + H = OH + OH$	0.71E+14	0.00	300
40	$H + O_2 = O + OH$	0.20E+15	0.00	16540
41	$O + H_2 = H + OH$	0.51E+05	2.67	6292
42	$O + H_2O = OH + OH$	0.30E+07	2.02	13400
43	$OH + H_2 = H + H_2O$	0.22E+09	1.51	3430

Historically, validations of detailed kinetic models have been done via simulations in homogeneous environments such as shock tubes or rapid compression machines, but simulations of the laminar flame structure have not been very useful as validation tests (Westbrook et al., 2009). In this sense, the validation of reduced mechanisms for a laminar flame becomes relevant.

The nature of a detailed chemical kinetic mechanism is intrinsically hierarchical (Dooley et al., 2008). Using this affirmation and beginning with species with only a few atoms, for which the reaction mechanism is often relatively simple, can be constructed mechanisms for larger fuel molecules.

Due to the lack of experimental data for MF diffusion flames and in order to validate the reduced mechanism, we proceed to compare the results with experimental data from Niemann et al. (2010). To approximate the energy flux in our model with the energy flux of experiments, it was considered two and a half molecules of MF per molecule of MB, setting what was called here as MF-surrogate. The Table 2 shows the relation of C , H and O for MF and for MB.

Table 2: Comparison of atomic contents of MF, MF-surrogate and MB.

Component	C	H	O
Methyl Formate	2	4	2
MF-surrogate	5	10	5
Methyl Butanoate	5	10	2

The temperature in the oxidizer stream, T_2 , is equal to $298K$, and in the fuel stream is $T_1 = 453K$. The initial mass fraction values for fuel and oxidizer are, respectively, $Y_{MF,1} = 0.09$ and $Y_{O_2,2} = 0.233$. The mass fraction of nitrogen corresponds to $Y_{N_2} = 1 - Y_{MF,1} - Y_{O_2,2}$. Results of numerical simulations are depicted as lines/symbols in the Figure 5.

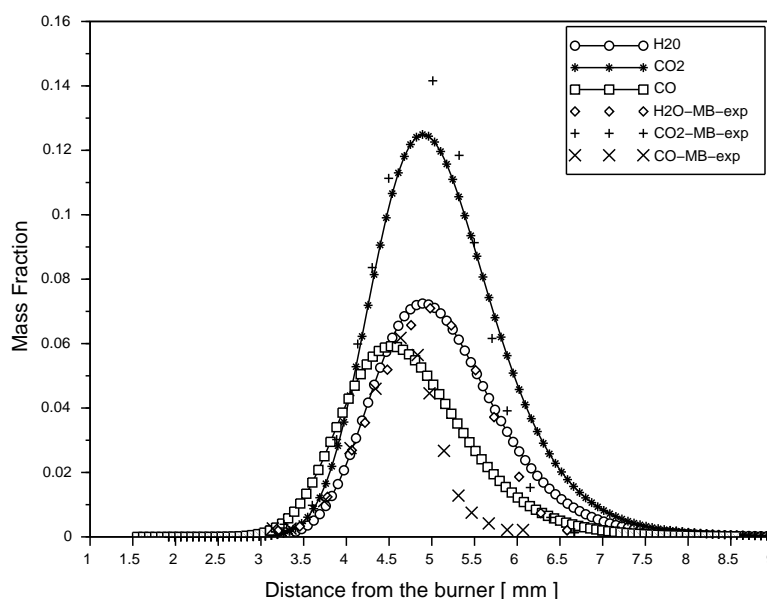


Figure 5: Major species calculated for MF-surrogate compared with the experiment for MB.

They reproduce the major products of combustion, i.e., CO_2 , H_2O and CO , measured within the flame. The error of numerical values compared to the experiment is of the order 15%. Comparison is not made with the full mechanism due to the stiff system of equations that results.

6 CONCLUSIONS

In this work, a reduced kinetic mechanism for the ester MF was developed. Starting with a 950 reactions and 176 species detailed mechanism, and using the techniques DRG, DFS and DSA, a reduced mechanism of 43 reactions among 23 species was developed. The main advantage of the reduced mechanism is the decrease of the computational work needed for solving the set of equations of the chemical system, a decrease of one order of magnitude for MF.

Results in progress indicate the existence of many interesting phenomena associated with flows involving mixing, reaction and combustion that are not yet fullness understood. The main contribution of this research is the understanding of some of these phenomena, which occur in the combustion of biofuels, for which reduced kinetic mechanisms are still under development in some known research centers in the area.

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